

Enhancements to the UK Photochemical Trajectory Model for Simulation of Secondary Inorganic Aerosol

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4 **ENHANCEMENTS TO THE UK PHOTOCHEMICAL**
5 **TRAJECTORY MODEL FOR SIMULATION OF**
6 **SECONDARY INORGANIC AEROSOL**
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26 **Abstract**

27 Particulate matter remains a challenging pollutant for air pollution control in the UK
28 and across much of Europe. Particulate matter is a complex mixture of which secondary
29 inorganic compounds (sulphates, nitrates) are a major component. This paper is
30 concerned with taking a basic version of the UK Photochemical Trajectory Model and
31 enhancing a number of features in the model in order to better represent boundary layer
32 processes and to improve the description of secondary inorganic aerosol formation. The
33 enhancements include an improved treatment of the boundary layer, deposition processes
34 (both wet and dry), attenuation of photolysis rates by cloud cover, and inclusion of the
35 aerosol thermodynamic model ISORROPIA II to account both for chemistry within the
36 aerosol and between the particles and gas phase. Emissions inventories have been
37 updated and are adjusted according to season, day of the week and hour of the day.
38 Stack emissions from high level sources are now adjusted according to the height of the
39 boundary layer and a scheme for generating marine aerosol has been included. The skill
40 of the improved model has been evaluated through predictions of the concentrations of
41 particulate chloride, nitrate and sulphate and the results show increased accuracy and
42 lower mean bias. There is a much higher proportion of the values lying within a factor of 2
43 of the observed values compared to the basic model and Normalised Mean Bias has
44 reduced by at least 89% for nitrate and sulphate. Similarly, the Index of Agreement
45 between calculated and measured values has improved by ~10%. Considering the
46 contribution of each enhancement to the improvement in the performance metrics, the
47 most significant enhancement was the replacement of the parameterisation of the
48 boundary layer height, relative humidity and temperature by HYSPLIT values calculated
49 for each trajectory. The second most significant enhancement was the parameterisation of
50 the photolysis rates by values calculated by an off line database accounting for the
51 dependence of photolysis rates on zenith angle, cloud cover, land surface type and column
52 ozone. The inclusion of initial conditions which were dependent on the starting point of the
53 trajectory and the modulation of stack emissions made the most significant improvement to
54 sulphate. Furthermore, in order to assess the model's response to abatement scenarios,
55 30% abatements of either NH_3 , NO_x or SO_2 showed a reduction in the sum of chloride,
56 nitrate and sulphate of between 3.1 % to 8.5 % (with a corresponding estimated reduction
57 of 1.6 – 3.7% reduction in PM_{10}). The largest reduction in this contribution is due to the
58 abatement of NO_x .

59 **Keywords:** Lagrangian model; sulphate; nitrate; chloride; Master Chemical Mechanism

60 Introduction

61 The United Kingdom, along with other European countries, is required to meet
62 stringent air quality standards for PM₁₀ and PM_{2.5}, as well as exposure reduction targets
63 for PM_{2.5} set by the European Union (EC, 2008). Abatement strategies to improve air
64 quality with respect to particulate matter (PM) pollution have considerable economic cost.
65 The Directive on “Ambient Air Quality and Cleaner Air for Europe” for example estimates
66 the cost of the ‘Maximum Technically Feasible Reduction’ scenario, abating SO₂, NO_x,
67 VOC, NH₃, and PM_{2.5}, to be € 39.7 billion per year in the year 2020. Additional measures
68 may be needed as there has been little change in annual mean concentrations of PM₁₀
69 since the year 2000 across considerable parts of Europe (Harrison et al., 2008, UN ECE
70 report on PM, 2007: <http://tarantula.nilu.no/projects/cccr/reports/cccr8-2007.pdf>).

71 Airborne particulate matter, be it expressed as PM_{2.5} or PM₁₀ mass, is a complex
72 mixture of chemical constituents. In the UK, the predominant individual constituents are
73 sulphates, nitrates and organic matter. Campaign data was collected in the months of May
74 and November of the years 2004 and 2005, in central Birmingham (Yin and Harrison,
75 2008), showing that sulphates and nitrates account on average for 34.5% of PM₁₀ and
76 45.2% of PM_{2.5} mass with the rest comprising of organics (PM₁₀; PM_{2.5} = 23.7%; 26.1%),
77 iron rich dust (PM₁₀; PM_{2.5} = 13.4%; 5.9%), elemental carbon (PM₁₀; PM_{2.5} = 8%; 11.2%),
78 sodium chloride (PM₁₀; PM_{2.5} = 9.3; 4%) and calcium salts (PM₁₀; PM_{2.5} = 7.4%; 2.5%).
79 During episodes of elevated PM concentrations exceeding the daily European Limit Value
80 of 50 µg m⁻³, the contribution of sulphates and nitrates increased to 57.2% of PM₁₀ and
81 68.5% of PM_{2.5} (Yin and Harrison, 2008) and were associated with transport of secondary
82 pollutants. Consequently, abatement of these components is potentially an attractive
83 policy option focussing on their precursor gases emitted by traffic, industry and domestic
84 sources (Erisman and Schaap, 2004, AQEG, 2005, Jones and Harrison, 2011).

85 Numerical models have an important part to play in predicting the impact of
86 abatement strategies and a number of such models have been used to predict
87 concentrations of particulate matter components within the European atmosphere. These
88 include Eulerian models such as LOTOS-EUROS (Schaap et al., 2008), CHIMERE
89 (Bessagnet et al., 2009), REM-CALGRID model (RCG) (Beekmann et al., 2007), and the
90 Unified EMEP model (Simpson et al. 2011) to name but a few. The unified EMEP model
91 has been used for policy development in Europe (Aas et al., 2007) to address regional
92 scale impacts of NO_x and SO₂ emission reductions on PM mass concentrations (despite
93 having uncertainties of about ± 40% for nitrate).

94 In the UK, the Photochemical Trajectory Model (PTM) has often been used to
95 understand boundary-layer pollution. For example, Walker et al. (2009) and Baker (2010)
96 simulated concentrations of ozone, and Derwent et al. (2009b) modelled concentrations of
97 sulphate and nitrate. The PTM is a boundary-layer Lagrangian model whose main
98 advantage over the Eulerian modelling approach is its ability to run highly comprehensive
99 chemical schemes without simplifications and parameterisations that may compromise the
100 performance of the chemical reaction scheme. The PTM is therefore suited to the
101 examination of abatement policies aimed at targeting emissions of individual precursors
102 (e.g. NH_3 , NO_x , SO_2). A number of studies have modelled particulate matter in Europe.
103 Most notably, the CityDelta project compared the ability of several models to predict the
104 impact of emissions reductions upon concentrations in European cities (Cuvelier et al.,
105 2007), specifically Berlin, Milan, Paris and Prague (Thunis et al., 2007). A subsequent
106 study (Stern et al., 2008) examined the ability of five chemical transport models to
107 reproduce PM_{10} episode conditions in central Europe. Model specific studies, such as
108 those with CHIMERE, have sought to simulate particulate matter concentrations in specific
109 parts of Europe, e.g. Portugal (Monteiro et al., 2007) and northern Italy (de Meij et al.,
110 2009). Air quality models used for calculating aerosol species over the UK include the
111 Community Multiscale Air Quality model (CMAQ), Chemel et al., 2010) and the Hull Acid
112 Rain Model (HARM), (Metcalf et al., 2005). CMAQ over-predicted O_3 and under-
113 predicted aerosol species with the exception of sulphate (Chemel et al., 2010). The
114 HARM and ELMO models (Whyatt et al., 2007) underestimated sulphate, nitrate and
115 ammonium by a large margin, and chloride massively. In the work of Redington and
116 Derwent (2002), the NAME model slightly under-predicted measured sulphate values
117 although the annual average values of nitrate compared well.

118 We have previously used the UK Photochemical Trajectory Model (a version of the
119 Derwent et al. (2009b) UK-PTM) to model concentrations of particulate sulphate and
120 nitrate in southern England and Northern Ireland in 2002 (Abdalmogith et al., 2006). While
121 our study was quite successful in modelling monthly mean concentrations and trends in
122 both nitrate and sulphate, it performed poorly in modelling daily concentration data,
123 especially during nitrate and sulphate episodes which were observed during easterly
124 transport trajectory events that brought high levels of particulate matter from Europe. It
125 was concluded that this was unlikely to be due to errors in the back trajectory alone and
126 that inclusion of a more sophisticated treatment of emissions and meteorology would
127 probably be required to address the issue adequately. It was also recognised that it would
128 be advantageous to: (i) use more than one photochemical back trajectory calculation for

each daily measurement, (ii) update emissions inventories and injection parameters to account for daily and seasonal variation; (ii) add wet deposition processes; (iii) replace the dynamic approach which treated the chemistry of the NH_4NO_3 – HNO_3 – NH_3 system as a bimolecular gas phase reaction with a more sophisticated thermodynamic algorithm, ISORROPIA II and (iii) and replace the clear-sky photolysis rates with ones which accounted for cloud cover.

Numerous amendments have been applied to the original model to form an enhanced UK-PTM with a view to providing an improved model aimed at addressing policymaking decisions. In this paper, we assess the changes resulting from the enhancements by using observed gas- and aerosol-phase data collected at the Harwell observatory in Oxfordshire, UK in 2007.

TECHNICAL DESCRIPTION OF THE MODIFICATIONS TO THE UK-PTM

The UK-PTM is a boundary-layer trajectory model originally assembled to simulate photochemical ozone production and subsequently used to derive Photochemical Ozone Creation Potentials (POCPs) (Derwent et al., 1998, Derwent et al., 2005). The model was initially set up to represent an idealised summertime photochemical episode occurring over the UK and used linear air mass trajectories. More recent studies have used air mass back trajectories calculated from meteorological wind velocity vector fields and a parameterised boundary layer height (Abdalmogith et al., 2006; Derwent et al., 2009b; Walker et al., 2009 and Baker, 2010). The changes made by these authors have improved the PTM. Here, we have modified the PTM further to include a new treatment of aerosol processes and of emissions from tall stacks, the effect of cloud cover on photolysis values, wet deposition, and a revised treatment of the emissions, amongst others. A complete list of changes made to the emissions inventories, chemical mechanism and back trajectory calculation is presented in Table 1.

Initial Conditions

An implicit assumption made in the original model (Abdalmogith et al., 2006) was that all trajectories, if they were extrapolated far enough back in time, would start over the Atlantic. The initial conditions were fixed to one set of values derived from a remote marine location off the west coast of the Republic of Ireland. In practice, 3-5 day back trajectories with arrival points in the UK do not all start over the Atlantic but may start over continental Europe. Stohl (1998) recommends that these trajectories are not further lengthened in order to maintain a reasonable level of certainty of their position. The

164 amended model uses 5 starting regions, namely Western, Northern, Eastern, Southern
165 and Central (Figure 1) to which initial concentrations of HCl, NO, NO₂, NO₃, HNO₃, SO₂,
166 SO₄, CO, CO₂, CH₄, HCHO, O₃, NH₃, NH₄⁺, NO₃⁻ and SO₄²⁻ were assigned (see Table S1
167 in Supplementary Information). These initial concentrations were derived from data
168 measured at Birkenes, Braganca, Campisabolos, Glashaboy, Hohenpeissenberg, Ispra,
169 Melpitz, Montelibretti, Norway Ocean Station, and S. Pietro Capofiume between 2000 and
170 2007. The initial concentrations were averaged over the measurements taken at a site
171 which best represented the conditions within the initial zone, e.g. for the Western or
172 Northern initial conditions, the most representative measurements are those collected at
173 Birkenes with back-trajectories crossing only over the ocean or the polar ice cap. There is
174 scope in the future to increase the number of starting zones and to make seasonal
175 adjustments to these values or to use concentration fields provided from larger domain
176 models.

177

178 **Meteorology**

179 The majority of studies use back trajectories with a timescale of 3-5 days. This is
180 generally a compromise between having sufficient time to describe the long-range
181 transport and the decreasing accuracy of individual back trajectories the further they are
182 projected backward in time (Stohl, 1998). In this work, four-day back trajectories were
183 calculated using the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory
184 (HYSPLIT-4) model (Draxler and Hess, 1998) and the archived NCEP/NCAR global data
185 assimilation system data (GDAS). The original UK PTM was simply based on three day
186 ECMWF back trajectories consisting of latitude/longitude values calculated online by
187 BADC.

188 An improvement in accuracy can also be achieved by averaging over the values
189 obtained from the output of more than one photochemical back trajectory for each daily
190 PM measurement. Instead of using a single trajectory with a specific arrival time e.g.
191 during the mid-afternoon at 15:00 h (as in the case of Baker (2010) who considered air
192 parcel trajectories arriving in Birmingham, UK), our model was adapted to run
193 photochemical calculations along trajectories for air masses arriving every hour of the day.
194 This implied that for each daily PM₁₀ filter measurement, an average calculated value was
195 determined based on meteorological conditions which were liable to change significantly
196 over the course of a day. Other multiple trajectory sampling schemes can potentially use
197 trajectories arriving at different heights and/or at many nodes of a gridded zone placed
198 symmetrically around the receptor site (private communication with R. Derwent, 2008).

In addition to latitude and longitude, other parameters are included in the back trajectory data, namely the boundary layer height, relative humidity and temperature. The HYSPLIT boundary layer heights give a more realistic description of the boundary-layer (BL) and replace the “clipped saw-tooth” function used in the earlier model of Abdalmogith et al. (2006) and shown in Figure S4 which is based on an idealised summertime episode. In particular, in HYSPLIT, the height of the mixing layer is taken as the height at which the potential temperature is at least two degrees greater than the minimum potential temperature. When plotted, the temporal boundary layer height profiles are no longer angular, they change more progressively and they are correctly synchronised to the rising and falling of the sun no matter at what latitude the air mass is located at. As the boundary layer expands, the constituents in the supra layer are mixed into the boundary layer and at dusk the supra layer concentrations are made equal to the boundary layer concentrations at dusk. However, as the boundary layer depth decreases, the constituents in the boundary layer are mixed back into the supra layer. There is no chemical evolution of the upper box.

Further auxiliary values in the back trajectory data included the 10 m wind velocity U_{10} and hourly rain rates f which were inputted into the parameterisation of sea salt flux and PM deposition respectively. Cloud cover and time/date data are also included so that the clear-sky assumption could be removed from the model and the emission flux corrections could be correctly synchronised to the hour of the day, day of the week and month of the year.

Chemistry

In order to include a more sophisticated treatment of aerosol properties (e.g. inclusion of ISORROPIA II) and to speed up the calculation, the Master Chemical Mechanism (MCM 3.1) was replaced with the Common Reactive Intermediate (CRI) mechanism (version CRI v02) developed by Jenkin et al. (2008). Jenkin et al. (2008) have shown that the CRI mechanism is virtually equivalent to the full MCM. This reduction in the number of species and reactions reduced the calculation time for one trajectory from one hour to approximately one minute. Watson et al. (2008) have made further reductions in the CRI mechanism by removing specific VOCs and reallocating the emissions to retained VOCs, but these reduced mechanisms were not included.

The VOC speciation used in this study is based on the speciated VOC emission inventory for 2000 compiled by Passant (2002) as part of the UK National Atmospheric Emission Inventory (NAEI) programme for the 2002 inventory year (the latest available at

the time of the original model development). This speciated emission inventory comprised 664 VOCs emitted from 249 source sectors with a total annual emission of 1543.7 ktonnes, including natural VOC emissions of 178 ktonnes per annum. The emissions from the 249 source sectors were aggregated to the relevant SNAP-1 sector. As many of the VOCs in the UK inventory were isomers or related to the model VOCs, the assignments were relatively straightforward.

In the original model, a clear sky scenario was always in place generally limiting the application of the model to summer conditions. The photolysis values J were parameterised to the solar zenith angle Z , using equation 1, where l , m , n , are constants available from the MCM website (<http://mcm.leeds.ac.uk/MCM>).

$$J = l(\cos Z)^m \exp(-n \sec Z) \quad (1)$$

In the enhancement, the photodissociation rates were calculated off line using the PHOTOL code (Hough, 1988). This has been updated to account for changes to spectroscopic and photochemical parameters, most notably the quantum yield of ozone (Atkinson et al., 1997). The input database contains the dependence of photolysis rates for 21 species on zenith angle, cloud cover, land surface type and column ozone. The local photolysis rates were derived during the model run by identifying the nearest element in the database. The aerosol and ozone columns were initially fixed, the latter at ~300 DU, but could be varied subsequently. The tabular values not only accounted for the solar zenith angle at a given time of the day, latitude and longitude, but also account for the surface over which the air mass travels (surface albedo of land, sea or ice) and the fractional cloud cover which was included as a field within the back trajectory data. Fractional cloud cover values were extracted, for each step of the trajectory, from Global Data Assimilation System (GDAS) forecast data generated by the National Weather Service's National Centers for Environmental Prediction (NCEP) (<http://ready.arl.noaa.gov/gdas1.php>). Using this system, values of photosynthetically active radiation (PAR) are also derived for the calculation of an environmental correction factor for monoterpenes and isoprenes calculated in the biogenic emission inventories (Figure S5).

262

263 **Aerosol Processes**

In the original UK-PTM, the aerosol chemistry was accounted for by a very simple process to represent the establishment of thermodynamic equilibrium in the NH_4NO_3 – HNO_3 – NH_3 system. Ammonia was rapidly combined with available aerosol sulphate to

form ammonium sulphate and any ammonia that remained was assumed to form a thermodynamic equilibrium with nitric acid and ammonium nitrate. No account was taken of hygroscopic water uptake which substantially affects the equilibrium. Furthermore, the formation of coarse mode aerosol nitrate was parameterised by the reaction of N_2O_5 and nitric acid with natural dusts and sea salt. Abdalmogith et al. (2006) and Derwent et al. (2009b) provide more details. The parameterisations based on the concentrations of the trace gases NH_3 , N_2O_5 , HNO_3 , and SO_3 have been replaced in the enhanced model by the aerosol thermodynamic equilibrium model for K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , NO_3^- , Cl^- , H_2O aerosols and associated gases, called ISORROPIA II (Fountoukis et al., 2009). In this work, it was compiled from FORTRAN code into a dynamic link library accessible by the FACSIMILE model. The complete theory of ISORROPIA II, together with a detailed description of the equations solved, the activity coefficient calculation methods and the computational algorithms used can be found in Nenes et al. (1998a,b) and Fountoukis and Nenes (2007).

281

282 **Aqueous Phase Processes**

The aqueous phase oxidation of SO_2 to H_2SO_4 in clouds is treated using a pseudo first-order process with a reaction constant R_k . The original value for R_k based on an assumed conversion of 1-2% / hour was replaced by a parameterisation based on relative humidity and cloud cover ε , (see equation 2 and Schaap et al. (2004)).

$$R_k = \begin{cases} 5.8 \times 10^{-5}(1 + 2\varepsilon), & RH < 90 \% \\ 5.8 \times 10^{-5}(1 + 2\varepsilon)[1.0 + 0.1 * (RH - 90.0)], & RH \geq 90 \% \end{cases} \quad (2)$$

287

288 **Deposition Values**

The conventional resistance approach - reviewed by Wesely and Hicks (2000) - of representing dry deposition processes was used in the model. The rate of dry deposition of the chemical species i , of concentration C_i , was given by,

$$\frac{d}{dt}[C_i] = -\frac{v_g}{H}[C_i] \quad (3)$$

where the boundary layer height and deposition velocity are represented by H and v_g respectively. For gases, tabulated dry deposition values were subdivided in the model to account for whether the air mass was over land or sea (see Table S2). For ozone, a more developed representation was used which accounted for the diurnal and seasonal variation induced by stomatal opening and closing. In the model, the approximation of the half sinusoidal function described by Hayman et al. (2010) was used. Further

improvements could be made by accounting for the opening and closing of stomata in response to the availability of moisture and the meteorological conditions. This adjusts the deposition value of ozone between a night time and winter constant value of 2 mm s^{-1} and a seasonal maximum ranging from 4 to 7 mm s^{-1} (Hayman, 2010).

For particulate matter (in this case for chloride, nitrate and sulphate particles) dry-deposition was accounted for by an expression developed by Smith et al. (1993) primarily for air masses as they move over the sea (equation 4),

$$V_d = \frac{V_t}{1 - \exp \left\{ - \left(\frac{V_t}{CD \cdot U_{10}} \right) \right\}} \quad (4)$$

This is a function of the 10 m wind speed U_{10} , the gravitational sedimentation velocity V_t and the Drag Coefficient CD , between the atmosphere and ocean (equation 5).

$$CD(U_{10}) = \begin{cases} 1.14 \times 10^{-3}, & U_{10} \leq 10 \text{ ms}^{-1} \\ (0.49 + 0.065U_{10}) \times 10^{-3}, & U_{10} > 10 \text{ ms}^{-1} \end{cases} \quad (5)$$

This expression (eq. 4) was used for land multiplied by a ratio of typical fixed land/sea values for $1 \mu\text{m}$ particles.

An additional loss term Λ_g , was added to represent removal by wet deposition using the parameterisation given by McMahon et al. (1979). This is a function of hourly rainfall f which was taken from the HYSPLIT back trajectory data (equation 6). The expression for SO_2 appears in equation 6, where f is the rainfall rate (mm h^{-1})

$$\Lambda_g = 17 \times 10^{-5} f^{0.6} \quad (6)$$

313

314 Emission Inventories

Emission fluxes were calculated using one of two sets of SO_2 , NO_x , NMVOC, CO and NH_3 emission inventories. For the UK land mass, NAEI emission data were used (<http://naei.defra.gov.uk/>). The NAEI inventory programme produces annual emission maps at $1 \text{ km} \times 1 \text{ km}$ spatial resolution for the major emission source sectors. These were aggregated to $10 \text{ km} \times 10 \text{ km}$ for each pollutant and major source sector. Emission data were taken from EMEP (<http://www.emep.int/>) for the remaining model domain. These were available on a $50 \text{ km} \times 50 \text{ km}$ grid for the same pollutants and major emission source sectors. The base year for the emissions was 2005 (the latest available at the time of the work), which were scaled to 2007 using the ratio of the national sector emission totals for 2005 and 2007 for each country. In a similar manner to that adopted by Hayman et al. (2010), a separate term was added to represent the emissions of VOCs from natural sources (taken to be trees), This is described further below.

327

328 *Emission fluxes*

329 Instantaneous emission fluxes were derived from the annual average emission
330 inventories for SO₂, NO_x, CO, NH₃, VOCs and NMVOCs and updated every 30 minute
331 trajectory step within the calculation as the air mass moved across the model domain. The
332 emissions were calculated from the annual emissions of NH₃, NO_x, VOCs, biogenic VOCs,
333 EC, and OC, scaled by factors describing diurnal, day-of-week, and monthly variations
334 which were published as part of the City-Delta European Modelling Exercise
335 (http://aqm.jrc.ec.europa.eu/citydelta/temp_factors_gh.txt)

336 *Biogenic emission fluxes*

337 Additional emission terms are added to the emission rate of isoprene and terpenes to
338 represent the natural biogenic emissions from European forests and agricultural crops.
339 The emission inventory used was that derived in the PELCOM project (PELCOM, 2000).
340 The inventory was aggregated to the EMEP 50 km x 50 km grid and gives emission
341 potentials for isoprene (from deciduous and evergreen trees: temperature and light-
342 sensitive), monoterpenes (from deciduous and evergreen trees: temperature or
343 temperature and light-sensitive) and other VOCs (OVOCs, from deciduous and evergreen
344 trees: temperature sensitive). The emission potentials were converted to local emission
345 rates using environmental correction factors (Guenther, 1997), derived from the
346 meteorological datasets. Hayman et al. (2010) compared the PELCOM emission
347 inventory with other estimates and discussed the implications of using this inventory.

349 *Sea salt emission flux*

350 In order to use ISORROPIA II, a sodium and chloride concentration were required
351 and this was derived from a sea-salt parameterisation developed by Gong (2003). Figure
352 S1 shows the flux distribution (equation 7) used to derive an injection term in the model
353 which was dependent on the wind speed at 10 m (U₁₀). This term was integrated into a
354 mass flux (using particle density to mass density relationship, $\frac{dm}{dr} = m_p \frac{dF}{dr}$) for all particle
355 radii r, reducing the parameterisation to a term involving just U₁₀,

$$\frac{dF}{dr} = 1.373u_{10}r^{-A}(1 + 0.057r^{3.45}) \times 10^{1.607e^{-B^2}} \quad (7)$$

356 For values of particle radius r and an adjustable parameter $\Theta = 30$, which controls the
357 shape of the sub-micron size distributions, the constants A and B are given by equations 8
358 and 9.

$$A = 4.7(1 + \Theta r)^{-0.017r^{-1.44}} \quad (8)$$

$$B = (0.433 - \log r)/0.43 \quad (9)$$

361 *Treatment of emissions from large stacks*

362 As the modelled air mass tracks along a trajectory, the emissions are entered
 363 independently of any height constraint into the boundary layer, suggesting a possible
 364 reason for the initially high SO₂ values (c.a. 2.5 times the expected value). Redington and
 365 Derwent (2002) also reported a similar problem with SO₂ concentrations calculated by
 366 their NAME model. The highest emissions of SO₂ on the emission maps were attributable
 367 to coal- and oil-fired power stations, together with other heavy industries (illustrated for the
 368 UK in Figure S3). Given that major industrial emissions are made via tall chimney stacks
 369 (100-300 m), there will be times of the day when the emissions are not made into the
 370 boundary layer but above it. Compared to state-of-the art 3-D models, where the
 371 emissions can be injected into the relevant model layer, this is a limitation of the boundary-
 372 layer model.

373 Bieser et al. (2011) calculated the vertical emission profiles of point-source emissions
 374 over Europe, evaluating an average effective emission height from plume rise calculations
 375 applied to various meteorological fields, seasons, times of the day and emission stack
 376 characteristics. In this work, an empirical equation (10) - approximating the findings of
 377 Bieser et al. (2011) - was derived by re-aggregating the calculated fractional values for the
 378 binned emission heights.

$$AFV(h) = \begin{cases} 0, & h < 144 \text{ m} \\ 0.45 + \tan^{-1}(1.02 * h - 310.6)/2.49, & 144 \text{ m} < h < 724 \text{ m} \\ 1, & h \geq 724 \text{ m} \end{cases} \quad (10)$$

379 where AFV(h) represents the mixing height (h)-dependent average fractional value of the
 380 emissions.

381 Using equation 10, the chimney code cuts the SNAP 1 NO_x and SO₂ emission fluxes
 382 by the fractional value AFV(h), if (i) the air mass passes over an emission square
 383 containing a major point source and (ii) the boundary layer height is less than 724 m, when
 384 it starts to slice the average emission plume.

385 The locations of emitting stacks were identified in the model using positional data
 386 published by the European Environment Agency's European Pollutant Release and
 387 Transfer Register (E-PRTR). (<http://prtr.ec.europa.eu/>) In total, 417 UK and 5171
 388 European NO_x and SO₂ emitters are accounted for in this way within the model. The
 389 inclusion of a "chimney code" attempts to overcome the limitation of a single box to

390 describe the boundary layer. As a result, the relatively high NO_x and SO₂ concentrations
 391 are reduced by 69% and 91% on average respectively relative to the base case of 11.18
 392 ppb and 2.43 ppb without the “chimney code”. Future model enhancements may well
 393 seek to account for the seasonal and daily activity of the power stations according to
 394 expected output.

395 The main local source of SO₂ and NO_x within the vicinity of the Harwell site is Didcot
 396 power station which is an 1.9 GW coal fired station used to meet peak demand. This is
 397 located 7 km downwind of Harwell for the prevailing south-westerly air masses, and it has
 398 been shown in a past study (Jones and Harrison, 2011) that Didcot power station has
 399 virtually no influence on the measurements at Harwell, and thus the SO₂ and NO_x
 400 emissions are reduced to zero for Didcot Power station in the model. This conclusion was
 401 drawn from data collected at Harwell from 2001 to 2008 and is thought to be due primarily
 402 to the lofting of the chimney emissions above the air sampled at Harwell.

403

404 **Computation**

405 The model was coded using the FACSIMILE numerical integration package (Curtis
 406 and Sweetenham, 1988). For each species *i* within the air parcel, its concentration within
 407 the boundary-layer C_i is governed by the differential equation (11)

$$\frac{d}{dt}[C_i] = P_i + \frac{E_i}{H} - L_i[C_i] - \frac{v_g}{H}[C_i] - ([C_i] - [B_i])\frac{1}{H}\frac{dH}{dt} \quad (11)$$

408 The source terms include the local emission rate from pollution sources E_i and the
 409 production rate of the species from photochemistry P_i . Similarly, the loss terms include the
 410 loss rate by photochemistry $L_i C_i$ and dry deposition rate $\frac{v_g}{H}[C_i]$. The effect of boundary
 411 layer height changes is represented by the time-dependent variable H . B_i is the
 412 concentration of the species in the supra boundary layer. The differential equations were
 413 solved using the variable order GEAR solver in the FACSIMILE software package.

414

415 **Model Validation**

416 The model was used to simulate a wide range of PM concentrations measured at the
 417 Harwell site in southern England (latitude = 51.571°N and longitude = 1.325°W). The
 418 primary test of the model was against daily concentrations of chloride, nitrate and sulphate
 419 collected at the Harwell site as part of the Airborne Particle Concentrations and Numbers
 420 Network (Hayman, 2008). The daily samples were collected using a Partisol 2025 sampler
 421 fitted with a PM₁₀ inlet. In addition hourly concentrations of NO, NO_x, CO and O₃ data were
 422 measured using chemiluminescence, IR Absorption and UV absorption respectively. The

data are verified and ratified every quarter using the results from independent QA/QC site audits (see link for more details http://www.airquality.co.uk/verification_and_ratification.php).

Other analytes were taken from other networks offering either a monthly or an hourly resolution. Monthly measured data was taken from the Acid Gas and Aerosol Network (AGANET) and the National Ammonia Monitoring Network (NAMN). These are two of the four components of the UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) network (<http://pollutantdeposition.defra.gov.uk/aganet>). The UKEAP measurements were carried out using the CEH DELTA (DEnuder for Long-Term Atmospheric sampling) system which is a low-cost diffusion denuder system that was originally developed for long-term sampling of ammonia and ammonium (Sutton et al., 2001), and which has also been tested for long-term sampling of acid gases (HNO_3 , HONO, HCl, SO_2) and aerosols (NO_3^- , NO_2^- , Cl^- , SO_4^{2-}) (Tang et al., 2008). Quality Assurance is maintained through the implementation of established sampling protocols, and monitoring of laboratory performance through participation in the EMEP and WMO-GAW inter-comparison schemes for analytical laboratories. The data quality is assessed using set Quality Control criteria: a) based on the capture efficiency using two denuders in the DELTA systems and b) involving the coefficient of variation for ammonia concentrations with the triplicate ALPHA samplers. Further details of the measurements and verification/ratification procedures are given in the annual reports to DEFRA (see link <http://www.uk-pollutantdeposition.ceh.ac.uk/reports>).

RESULTS

Generalisation of the Patterns Observed in the Daily Back Trajectories

Data from the period 19 March 2007 to 18 May 2007 were used for the validation capturing a large range of PM_{10} values to model. The patterns observed in the measured daily PM values can be accounted for by how the 24 hourly back trajectories (for the measurement day) spread across the emission map (see Figure S6). At the start of the sampling period (19th March) an increase – from relatively small concentrations - in the nitrate and sulphate values - was observed after the third day (Figure 2). This is accounted for by the air mass trajectories switching their origins from over the North Pole (passing directly down through Scotland and Northern England to the receptor site on 20/03/2007) to an origin in Eastern Europe on 25th March (25/03/2007 in Figure S6). The air masses continued to originate from eastern Europe up until 2nd April (03/04/2007) after which the starting points of the trajectories move towards the North Sea and then towards

the Atlantic off the coast of Republic of Ireland and France between 3rd and 14th April (09/04/2007). From 15th April to 5th May the trajectories start at locations close to the west and east coast of the UK, crossing over France, Germany and Denmark periodically (15/04/2007). Then in the final phase of the sampling period 6-19th May, the air masses have their origin firmly in the middle of the Atlantic Ocean (18/05/2007). In general, when the air mass spends most of its time over the sea, the chloride measurements are high and the nitrate and sulphate are low (see Figure 2). Conversely, when the air mass originates over land and passes mainly over land, then the chloride measurements are low and the nitrate and sulphate measurements are high, consistent with the clustered back trajectory measurements of Abdalmogith and Harrison (2005). When considering the time series of predicted and modelled chloride, nitrate and sulphate, the model output impressively tracks the measured nitrate values. Similarly, the modelled sulphate values satisfactorily track the measured values but with a high degree of scatter shown by the plotted hinges. The performance of chloride is not as impressive but is acceptable when considered in the context of the range of modelled values with nitrate and sulphate.

Model Verification and Validation

Table 2 compares the simple statistical values calculated for the gases $\text{NH}_{3(g)}$, HNO_3 , SO_2 , HCl , CO , NO , NO_2 and O_3 and the aerosol components NH_4^+ , Cl^- , NO_3^- , SO_4^{2-} , for the period 02/04/2007 to 30/04/2007, across which the average temperature and relative humidity were 11°C and 72 % respectively. This period corresponds to the monthly denuder and aerosol filter measurement for April made on the Acid, Gases and Aerosol Network (AGANET). Considering the core functionality of the enhanced-PTM in predicting ozone, the model under-predicts O_3 , NO and NO_2 by 20%, 64% and 46% although the ratio of NO_2 to NO is similar for both modelled and measured values.

The enhanced model under-predicts mean values of ammonia gas, ammonium, nitric acid and hydrochloric acid by 12 %, 0 %, 88 % and 96 % respectively. In the original model, there was an overestimation of sulphur dioxide as also reported by Redington and Derwent (2002). By using the height dependent emission of SO_2 , prescribed in the chimney code, we have brought this prediction down from a mean value of 2.43 ppb to a mean value of 0.27 ppb. With regards to the particulate matter concentrations, the model over-predicts the measured value of chloride, nitrate and sulphate by 20 %, 8.1 % and 18% respectively. Although these discrepancies appear large, the model results appear more reasonable when comparing with the full time series (Figure 2 & 3).

492 The improvement in the capability of the enhanced PTM to model nitrate and
493 sulphate can be judged from Figure 2 where a comparison with the original model output is
494 presented. Both original and enhanced modelled values of nitrate and sulphate do indeed
495 span the range of measured values for the sampling period considered but the original
496 model fails to account for specific scenarios thus leading to a short-fall in the calculated
497 nitrate and sulphate values. The original model did not calculate chloride but the
498 comparison shows that the enhancements made to the model address the general under
499 prediction of nitrate and sulphate. The original PTM was capable of modelling the more
500 significant nitrate and sulphate episodes associated with easterly back trajectories but
501 failed to account for the smaller episodes resulting from westerly trajectories. This led to
502 sharp increases in nitrate and sulphate when the air masses switched from westerly to
503 easterly (14/04/2007-15/04/2007). The enhanced model accounts better for the high
504 values observed during the nitrate episodes, especially the episode between 25th and 27th
505 March where the nitrate value reached 36 $\mu\text{g m}^{-3}$. This episode was initially thought to be
506 due to the presence of fog, although the meteorology measured at the nearby met-station
507 of Benson did not indicate this to be the case. However, weather diaries for these three
508 days record the UK weather as being generally dry by day due to an anticyclonic ridge,
509 which can be associated with overnight fog. (see link:
510 <http://www.met.rdg.ac.uk/~brugge/diary2007.html>). The trajectories for this period
511 originated over central and eastern Europe thus leading to the observed sulphate episode.
512 The enhanced model also reflected, but over-predicted, later sulphate episodes
513 (12/04/2007-18/04/2007 and (20/04/2007-24/04/2007). Whereas the original model
514 represented this episode by a brief spike in the sulphate values, the new model, which is
515 able to model episodes due to westerly air masses, shows a longer episode better
516 matching the measured data.

517 A direct comparison of the calculated and measured data is shown in Figure 3 where
518 the time-series data has been replotted. The poor performance of the model to account
519 for chloride can be immediately seen by the large fraction of points which are respectively
520 either above or below the marked 2:1 or 1:2 boundary. Although the general trend is
521 correct, there is a significant amount of scatter about the fitted and 1:1 line showing that
522 there is a weakness in the modelling of chloride to be accounted for. The plots for nitrate
523 and sulphate are much better with the majority of points within the 2:1 and 1:2 boundary.
524 The over-prediction of sulphate results in a larger than unity gradient for sulphate, and the
525 less than unity gradient of nitrate suggest the model is still slightly under-estimating the

526 higher values seen during the episodes.

527 Even though some of the higher measured chloride values are under-predicted, the
528 temporal trends predicted by the model reflect the measured values fairly well as seen in
529 Figure 2. This gives confidence in the ability of the Gong parameterisation and
530 ISORROPIA II parameterisation to model the correct magnitude of sea salt, although the
531 measured value was in general within or just outside of the max/min modelled values.
532 This large discrepancy may be accounted for by uncertainties in the trajectory values of 10
533 m wind speed. Good results are obtained for nitrate for which the median daily value was
534 much closer to the PM value. With regards to sulphate, the PTM was able to model
535 correctly both high and low sulphate episodes although with a very high scatter of values
536 as depicted by the max/min point of the plotted hinges. Also, there were periods where
537 sulphate was significantly over-predicted.

538 Table 3 considers the effect of the model enhancements - measured against the daily
539 observed PM measured values - using performance metrics calculated separately for the
540 original and enhanced UK-PTM. The complete 61 day measurement period was
541 considered for this comparison and the enhanced model improves considerably the
542 average calculated values for the period. Both nitrate and sulphate were under-predicted
543 relative to the observed values by 56% using the original model. The enhancements
544 reduced this discrepancy for nitrate and sulphate to within 1.5% and 3.3% of the measured
545 mean values and the calculated chloride value was within 13% of the measured value.
546 Furthermore, improvements in how well the calculated values track with the measured
547 values are reflected in the values of Spearman's correlation coefficient r which increase
548 from approximately 0.5 to 0.83 and 0.65 for nitrate and sulphate respectively. As Figure 3
549 also indicates, the correlation coefficient of 0.5 for the chloride values shows that the
550 model does not estimate chloride as well as it calculates nitrate and sulphate.

551 The Root Mean Square Error, RMSE provides information on the short term
552 performance and has a possible range from 0 to $+\infty$ (Derwent 2009a). Again, the closer
553 this value is to zero the better is the short term performance and although fractional values
554 are not achieved using the enhanced model and we do not better the values of Derwent et
555 al. (2009b) modelling longer time series measurements at Harwell with a UK-PTM, a
556 considerable improvement in the short term performance of the PTM can be seen in our
557 enhanced model. The Index of Agreement, IA, reflects the improvement in performance.
558 IA is a statistical measure of the correlation of the predicted and measured concentration;
559 the closer this is to 1 the better the correlation. For nitrate and sulphate an increase in the

560 value of IA is observed from 0.88 and 0.86 to 0.96 and 0.95 respectively. The value of IA
561 for chloride is also unexpectedly high considering the values of Spearman correlation
562 coefficient (r). As argued by Nath and Patil (2006) the value of r is often misleading as it
563 may be unrelated to the size of difference between observed and predicted values, and
564 that IA is better measure of how two values track each other over a period of time.

565 The improvement in the calculation of nitrate and sulphate is reflected also in the
566 improved value of the mean bias error MB. The Mean Bias, MB provides information on
567 the long term performance and has a range between the negative of the mean observed
568 value to $+\infty$. The closer this value is towards zero the better the long term performance.
569 For both nitrate and sulphate the MB value is reduced to fractional values implying that the
570 model's long term performance is improved. The fractional MB value for chloride also
571 indicates that the model's long term performance in calculating chloride is comparable to
572 that of nitrate and sulphate. Considering the Normalised Mean Bias (NMB) values, if these
573 lie between -0.2 and 0.2 then the model is acceptable according to the recommendation of
574 Derwent et al. (2009a). For the case of the nitrate and sulphate values respectively, the
575 values decrease in magnitude from -0.59 and -0.58 respectively using the original model to
576 0.05 and -0.07 for the enhanced model (cf the average values of Derwent et al. (2009a) of
577 0.05 and 0.14 for the whole year). The NMB value of -0.1 for chloride indicates that the
578 model's performance is acceptable but far from ideal. This is also reflected by the fraction
579 of the calculated chloride concentrations FAC2, within a factor of two of the observed
580 values, being just less than 50 %. For nitrate and sulphate this FAC2 value is 77 % and 81
581 % respectively. Using the original model the fraction of calculated nitrate and sulphate
582 values within a factor of 2 of the observed values was 18% and 11% respectively.

583 The contribution of each enhancement can be judged in Table 4. In this, the results
584 from the enhanced model are compared with the chloride, nitrate and sulphate values
585 when each enhancement is restored to its original setting. For each case, the decrease in
586 performance is represented by each percentage. Considering the percentage change in
587 the arithmetic means, the significance of the enhancements has been ranked from top to
588 bottom in the table. The most significant enhancement for chloride, nitrate and sulphate is
589 observed when the replacement of parameterisation of temperature, relative humidity and
590 the boundary layer height by values modelled by HYSPLIT. This is closely followed by the
591 enhanced photolysis values for just chloride and nitrate and then by the inclusion of
592 ISORROPIA II and cloud cover in the model for nitrate. The enhancement of the liquid
593 phase oxidation of SO_2 to H_2SO_4 in clouds by equation 2, inclusion of stack height
594 dependent emissions and the improvement in the initial conditions contribute most to the

595 sulphate enhancement. These trends are also observed with the percentage change of
596 the NMB values and in the context of a limit of acceptability of ± 0.2 , the largest changes
597 were seen for sulphate. Similar comparisons were made for FAC2 and r^2 and although the
598 changes were not as significant, again, the maximum changes were observed for
599 sulphate.

600 For policymaking decisions, Derwent et al. (2009b) showed that a 30% abatement of
601 either NH_3 , NO_x or SO_2 led to at least 3.5% reduction of either nitrate or sulphate.
602 Reducing NH_3 by 30% reduced nitrate and sulphate by 12.2% and 0% respectively
603 compared to a 14.8% and 2.3% reduction when abating NO_2 (Derwent et al., 2009b). The
604 abatement of SO_2 yielded the highest reduction (of 14.8%) of the contribution of sulphate
605 to the PM value. The abatement of CO had no effect on the PM contribution from
606 ammonium, nitrate or sulphate. Likewise, the abatement of VOCs reduced the
607 contribution to PM from ammonium, nitrate and sulphate by 0 %, 2.1 % and 0.6 %
608 respectively. Referring to Table 5, our model shows comparable findings. Abating NH_3 by
609 30 % reduced nitrate and sulphate by 5.1 % and 0.1 % respectively. Similarly, lowering
610 NO_x by 30 % reduced nitrate and sulphate by 17.7 % and 1.9 % respectively. The 30 %
611 abatement of SO_2 yielded the highest reduction (by 20.8 %) of the contribution to the PM
612 value via sulphate and 2.5% of nitrate. For NO_x and SO_2 , our enhanced model predicts a
613 larger reduction of nitrate and sulphate respectively, compared to Derwent et al. (2009b)
614 suggesting that our enhancements are potentially accounting for additional sensitivity to
615 the abatement of these precursors. The model suggests that the abatement of any of NH_3 ,
616 NO_x , or SO_2 by 30% will lead to a reduction in the sum of SO_4^{2-} , NO_3^- and Cl^- of between
617 3.1 % to 8.5 %, with the largest reduction due to NO_x abatement.

618

619 SUMMARY

620 Modifications to the UK Photochemical Trajectory model have been made in order to
621 make the chemical and meteorological processes more representative of the actual
622 conditions leading to the composition of the air masses sampled. The principal aim of this
623 work has been to model values of chloride, nitrate and sulphate over a fixed period of time
624 where a varied range of hourly nitrate values have been encountered resulting from air
625 mass trajectories with origins both over sea and continental Europe. Although the full
626 episodic trends of nitrate have not been totally accounted for by the enhancement, the
627 nitrate, sulphate and chloride have been modelled far more satisfactorily in comparison to
628 the original model.

629 When the original and enhanced UK-PTM are evaluated against the criteria
630 established by Derwent et al. (2009a) for deciding the adequacy of models for policy
631 relevant queries, we observe a general improvement in the performance metrics. The
632 largest improvement is seen for the nitrate concentration with the mean bias falling to well
633 below 0.05 with 77 % of the values lying within a factor of two of the observed values. The
634 calculations of sulphate had a mean bias of 0.07, and 88 % of the values lay within a factor
635 of two of the observed values. The calculation of chloride however needs improvement
636 having a normalised mean bias of -0.1 with 42 % of the calculated values lying within a
637 factor of two of the observed values. In general, the original model under predicted the
638 average observed values by 55% and using the enhancements the model calculates
639 nitrate and sulphate to within 1.5% and 3.3% of the mean measured values. Furthermore,
640 the enhancements have improved the correlation between the calculated and measured
641 values reflected by the increase in the Index of Agreement from 0.88 and 0.86 to 0.96 and
642 0.95 for nitrate and sulphate respectively. Similarly, improvements in the model's ability to
643 represent the long and short term trends in both nitrate and sulphate have been
644 demonstrated by the lowering of the values of the normalised mean bias and root mean
645 square error towards the preferred values of zero. Our model indicates that a 30%
646 abatement of either NH_3 , NO_x or SO_2 , will lead to a reduction in the sum of chloride, nitrate
647 and sulphate of between 3.1 % to 8.5 % (with a corresponding estimated reduction of 1.6 –
648 3.7% reduction in PM_{10}). The largest reduction in this contribution is due to the abatement
649 of NO_x .

650

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873 TABLES LEGENDS

874 Table 1. Summary of changes made to the UK-Photochemical Trajectory Model.

875
876 Table 2. Simple statistics calculated using modeled and measured concentrations
877 collected over the period from 02/04/2007 to 30/04/2007. Mean temperature
878 $284.3 \pm 2.3\text{K}$ and relative humidity of $71.8 \pm 6.7\%$. [* Values represent the
879 measured monthly value only. ** The O_3 values represent the period when
880 measured values were available, from 26/04/2007 to 19/05/2007.]

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882 Table 3. Model performance metrics for the period from 19/03/2007 to 19/05/2007 using
883 full days data. [N = number of complete pairs of measured and calculated
884 values; MB = mean bias ($\mu\text{g}/\text{m}^3$); NMB = Normalised mean bias; MGE = mean
885 gross error; NMGE = normalised mean gross error; FAC2 = A count fraction of
886 points within 0.5 and 2 times the observation; RMSE = root mean square error
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894 abatement (by 30%) on the calculated chloride, nitrate and sulphate
895 concentrations. A comparison is made with the study of Derwent et al. (2009) –
896 abatement figures shown in italics.

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900 Figure 1. Boundaries separating the Northern, Eastern, Southern, Western and Central
901 Regions of Europe. Initial concentrations are specified for each region and are
902 used as initial conditions in each calculation depending on which region the
903 trajectory starts.

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906 sulphate. Measurements (black line) were made with a Rupprecht and
907 Patashnick Partisol 2025 sampler with PM_{10} sampling inlet. The calculated data
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909 24 hourly calculated values. The middle horizontal line represents the median;
910 the two hinges represent the first and third quartile; and the two whiskers
911 represent the maximum and minimum values. Also included are the results
912 shown by the brown line from the initial PTM model. (Referring to Figure 1, the
913 coloured ribbon at the bottom of each plot shows the zone from which the
914 trajectory used in the calculation started.)

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919 Axis method (Ayers, 2001), indicated by the solid black line and equation. Also
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921 out by the blue line and the boundaries where the calculated values are twice or
922 half the value of the measured values (dashed lines).

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Table 1. Summary of changes made to the UK-Photochemical Trajectory Model.

	Enhancement of	TO	FROM
Emissions	Continental VOC/NO _x /CO/SO ₂ /Biogenics/NH ₃	EMEP, base year 2005 (50×50 km)	CORINAIR, base year 1985 (150×150 km)
	United Kingdom VOC/NO _x /CO/SO ₂ /Biogenics/NH ₃	NAEI, base year 2005, (10×10 km)	CORINAIR, base year 1985 (10×10 km)
	Sea Salt flux	Gong (2003) parameterisation	None present
	Boundary layer / free troposphere injection	B.L. height determines input of SO ₂ and NO _x .	None present
	Initial Conditions	Dependent on initial lat/long position being in either a N/E/S/W or Central Region.	Westerly Clean conditions for all trajectories
Chemical Mechanism	Gas phase	cri-v02	MCM
	Aqueous phase	ISORROPIA II	None present
	Aqueous oxidation of SO ₂ , Photolysis Rates	Schaap et al. (2004) Dependent of lat/long, cloud cover and surface.	None present Based on a parameterisation.
	Gaseous dry deposition Rates	Dependent on surface (land/sea)	Fixed values
	NO ₂ & SO ₂ wet deposition Rates	McMahon et al. (1979) parameterisation	None Present
	PM deposition rates	Smith et al. (1993) parameterisation	None present
Back Trajectory Calculation	Lat/Long	Calculated using HYSPLIT	Calculated using BADC
	Mixing Depth	Calculated using HYSPLIT	Saw tooth fn
	Temperature	Calculated using HYSPLIT	Sinusoidal fn
	RH	Calculated using HYSPLIT	Sinusoidal fn
	Cloud Cover	Calculated using HYSPLIT	None present
	U10	Calculated using HYSPLIT	None present
	Rain	Calculated using HYSPLIT	None present
	(YY/MM/DD/HH/MM)	Calculated using HYSPLIT	None present

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Table 2. Simple statistics calculated using modeled and measured concentrations collected over the period from 02/04/2007 to 30/04/2007. Mean temperature 284.3 ± 2.3K and relative humidity of 71.8 ± 6.7 %. [* Values represent the measured monthly value only. ** The O₃ values represent the period when measured values were available, from 26/04/2007 to 19/05/2007].

Const- ituent	Unit	Field Values					PTM Values				
		Min.	Lower quartile	Geo. Mean	Upper quartile	Max.	Min.	Lower quartile	Geo. Mean	Upper quartile	Max.
NH _{3(g)}	ppb	-	-	6.95	-	-	0.14	3.95	6.11	9.8	22.1
NH ₄ ⁺	μg/m ³	-	-	2.80	-	-	0	0	2.80	5.05	16.9
HNO ₃	ppb	-	-	0.59	-	-	0	0.02	0.07	0.28	2.3
SO ₂	ppb	-	-	0.99	-	-	0.02	0.12	0.27	0.63	15.9
HCl	ppb	-	-	0.26	-	-	0	0	0.01	0.04	0.99
Cl ⁻	μg/m ³	0.13	0.26	0.56	1.10	3.40	0	0.43	0.67	1.42	4.16
NO ₃ ⁻	μg/m ³	2.17	4.56	6.89	10.7	16.4	0.05	4.62	7.45	13.9	35.7
SO ₄ ²⁻	μg/m ³	1.21	2.42	3.62	5.33	9.92	0.48	1.59	4.27	9.39	67.8
CO	ppb	-	-	-	-	-	123.6	150	177.1	200.8	528.5
NO	ppb	0.00	0.00	1.20	2.20	18.8	0.0	0.03	0.43	2.64	115.0
NO ₂	ppb	0.00	3.67	7.03	9.98	37.1	0.47	2.46	3.78	5.93	20.2
O ₃ ^{**}	ppb	7.6	24.4	28.7	36.7	62.1	0	15.8	23.0	28.4	46.3

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Table 3. Model performance metrics for the period from 19/03/2007 to 19/05/2007 using full days data. [N = number of complete pairs of measured and calculated values; MB = mean bias ($\mu\text{g}/\text{m}^3$); NMB = Normalised mean bias; MGE = mean gross error; NMGE = normalised mean gross error; FAC2 = A count fraction of points within 0.5 and 2 times the observation; RMSE = root mean square error ($\mu\text{g}/\text{m}^3$); r = Spearman's correlation coefficient; and IA = Index of Agreement.]

	<i>Chloride</i>	<i>Nitrate</i>	<i>Sulphate</i>
Observed Values			
<i>Arithmetic Mean</i>	1.10	6.75	3.90
<i>St dev</i>	1.02	6.23	2.60
Original Model Values			
<i>Arithmetic Mean</i>	-	2.96	1.73
<i>St dev</i>	-	4.99	4.11
<i>N</i>		58	58
<i>MB</i>	-	-3.93	-2.24
<i>MGE</i>	-	5.10	3.33
<i>NMB</i>	-	-0.59	-0.58
<i>NMGE</i>	-	0.76	0.86
<i>RMSE</i>	-	6.80	4.43
<i>FAC2</i>		0.18	0.11
<i>r (Spearman)</i>	-	0.57	0.55
<i>IoA</i>	-	0.88	0.86
Enhanced Model Values			
<i>Arithmetic Mean</i>	0.96	6.85	4.03
<i>St dev</i>	0.52	5.10	3.33
<i>N</i>	57	57	57
<i>MB</i>	-0.11	0.32	0.28
<i>MGE</i>	0.78	2.47	1.82
<i>NMB</i>	-0.10	0.05	0.07
<i>NMGE</i>	0.71	0.36	0.47
<i>RMSE</i>	1.06	3.94	2.51
<i>FAC2</i>	0.42	0.77	0.81
<i>r (Spearman)</i>	0.27	0.83	0.65
<i>IA</i>	0.9	0.96	0.95

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944 **Table 4. Observed changes in values of the Performance Metrics when each enhancement**
 945 **in the model is restored to its original setting.**
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<i>Enhanced Model Values minus...</i>	<i>Δ (Arithmetic Mean)</i>			<i>Δ NMB</i>		
	<i>Cl⁻</i>	<i>NO₃⁻</i>	<i>SO₄²⁻</i>	<i>Cl⁻</i>	<i>NO₃⁻</i>	<i>SO₄²⁻</i>
<i>HYSPLIT temp, RH, BLH values</i>	14%	10.0%	-8.2%	-0.08	-0.18	0.00
<i>Enhanced photolysis rates</i>	-7.4%	-17%	-0.5%	0.15	0.12	-0.09
<i>ISORROPIA II</i>	-	8.0%	0.9%	0.11	0.09	0.01
<i>Aqueous oxidation of SO₂,</i>	2.1%	2.7%	-30%	0.01	0.03	-0.33
<i>Trajectory dependent initial conditions</i>	4.3%	-0.3%	-26%	-0.02	-0.01	0.22
<i>NO₂ and SO₂ Stack height dependent emissions</i>	-2.1%	-1.9%	14%	0.03	0.00	-0.29
<i>Cloud cover dependent photolysis rates (sunny day scenario)</i>	-1.1%	6.4%	0.9%	-0.01	0.07	0.01

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 950 **Table 5. Change of calculated species concentrations (%) resulting from precursor**
 951 **abatement (by 30%) on the calculated chloride, nitrate and sulphate concentrations. A**
 952 **comparison is made with the study of abatement figures shown in italics.**
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Precursor Abated	<i>Chloride</i>	<i>Nitrate</i>	<i>Sulphate</i>	Σ (chloride + nitrate + sulphate)	<i>PM₁₀</i>
<i>NH3</i>	-2.2	-5.1 (-12.2)	0.1 (0)	-3.1	-1.6
<i>NOx</i>	-0.6	-17.7 (-14.8)	1.9 (2.3)	-8.5	-3.7
<i>SO2</i>	0.8	2.5 (3.5)	-20.8 (-14.8)	-6.1	-2.3

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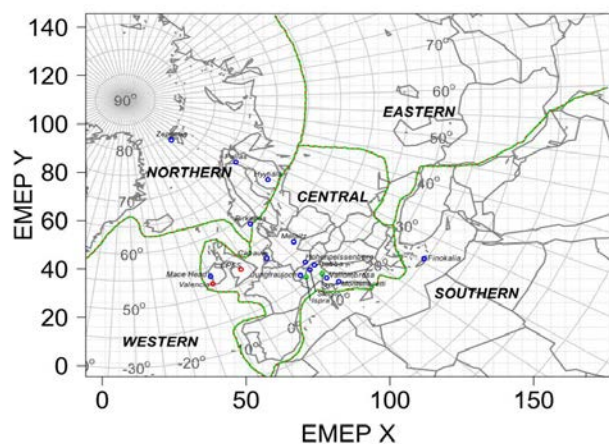
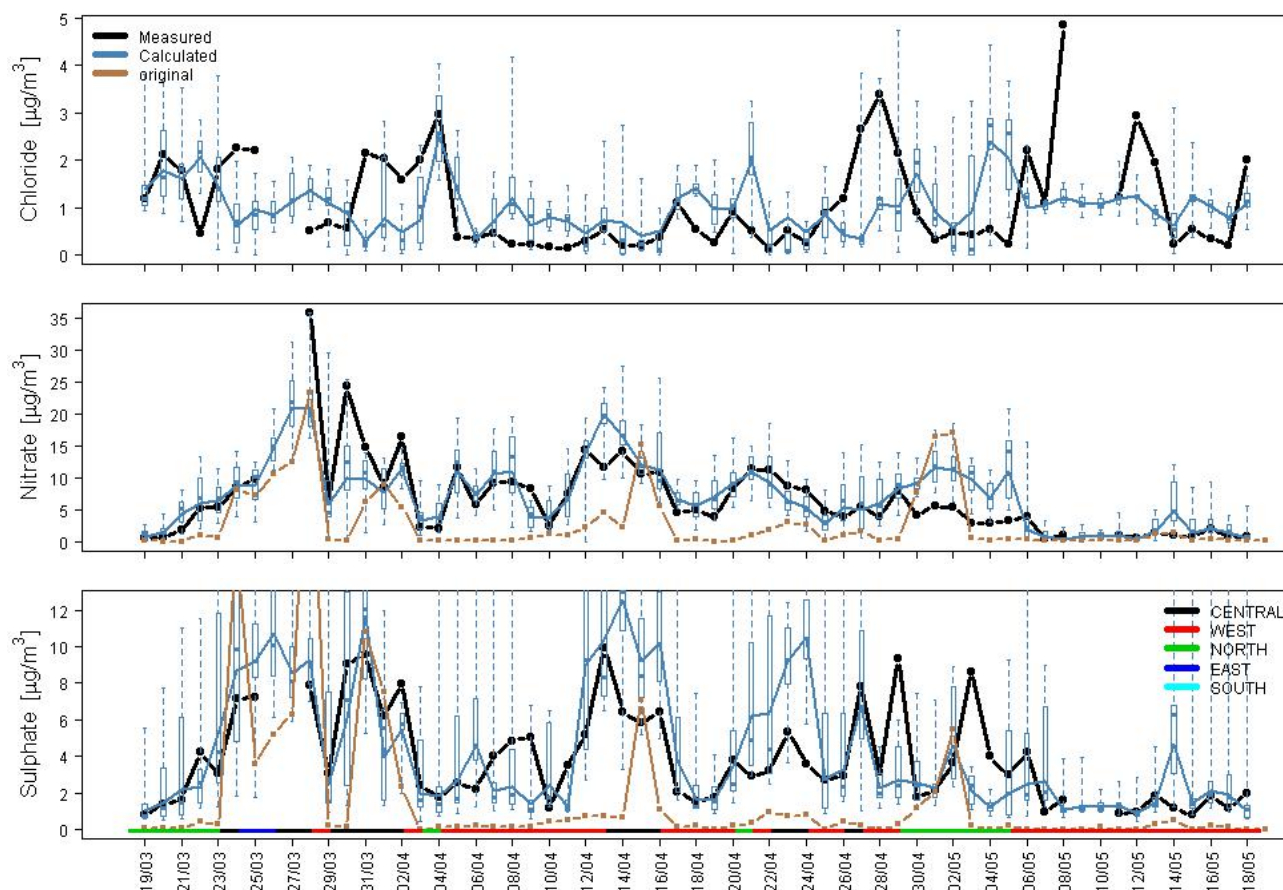


Figure 1. Boundaries separating the Northern, Eastern, Southern, Western and Central Regions of Europe. Initial concentrations are specified for each region and are used as initial conditions in each calculation depending on which region the trajectory starts.



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Figure 2. Comparison between calculated and measured PM₁₀ chloride, nitrate and sulphate. Measurements (black line) were made with a Rupprecht and Patashnick Partisol 2025 sampler with PM₁₀ sampling inlet. The calculated data is depicted by the blue whisker plots derived from the statistics of each group of 24 hourly calculated values. The middle horizontal line represents the median; the two hinges represent the first and third quartile; and the two whiskers represent the maximum and minimum values. Also included are the results shown by the brown line from the initial PTM model. (Referring to Figure 1, the coloured ribbon at the bottom of each plot shows the zone from which the trajectory used in the calculation started.)

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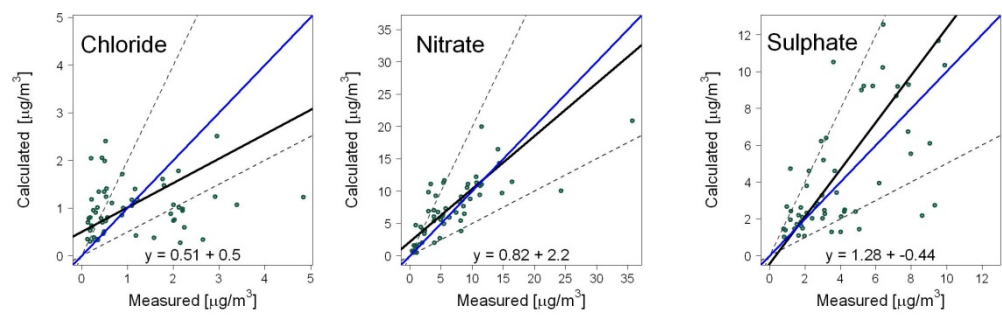


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